INTERPRETING COAL DEVOLATILIZATION AS A FLASH DISTILLATION DRIVEN BY COMPETITIVE KINETICS FOR DEPOLYMERIZATION AND REATTACHMENT

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Introduction

According to the most recent theories[1-4], the evolution rates, distribution, and molecular characteristics of the volatile products of coal devolatilization express the independent influences of chemical reaction rates and macromolecular configuration. Generally speaking, these approaches firm up the connections between the modeling species associated with the reactant and coal's structural features and functional groups inferred from chemical analyses. Obviously such connections are essential to systematic interpretations of the behavior of various coals. But chemical kinetics and configurational probabilities alone cannot account for the reduced tar yields and smaller tar fragments from devolatilization at elevated pressures. Reduced tar yields have long been attributed to redeposition of tar from the gas phase on the time scale for transport of volatiles through the particle surface, although an alternate scheme[5] based on flash distillation correlates yields as well as tar molecular weight distributions (MWDs) without invoking any finite-rate, mass transport mechanism.

The theory introduced in this paper extends the development of models based on chemical kinetics, macromolecular configuration, and flash distillation, and is called FLASHCHAIN. Like DISCHAIN[1] and DISARAY[2], it comprises simplified kinetic mechanisms and analytical expressions to account for configurational effects, and to describe their evolution in time. However, the complete size distributions of all fragments are now determined. And like FLASHTWO[5], this theory invokes a phase equilibrium among intermediates in the condensed phase and tar components in the vapor to rationalize the pressure dependence. Whereas the fragment distribution in FLASHTWO is assumed a priori, it is now computed from the configurational model.

In the sections which follow, the main features of the theory are outlined briefly, largely to explain the various modeling parameters. Then model correlations are presented for the devolatilization of high volatile bituminous coals, including the proportions of tar and noncondensible gases, and tar molecular weights for broad ranges of temperature, heating rate, reaction time, and pressure.

Overview of the Theory

Coal is modeled a distribution of linear chains composed of refractory aromatic nuclei interconnected pairwise by two types of linkages, labile bridges and refractory char links. The initial coal constitution is specified by the proportions of labile and broken bridges and char links, and the probability that peripheral groups appear on the ends of fragments. Initially and throughout pyrolysis, the condensed phase species are subdivided into reactant, intermediate, and metaplast lumps, in order of decreasing size.

Although the cutoff sizes are arbitrary, their proportions are described by analytical expressions for the complete size distribution as a function of the instantaneous numbers of bridges, char links, and ends. Consequently, for the initial coal reactant species, the sizes in the fragment distribution shift toward smaller values as the initial fraction of broken bridges is increased, and more of the coal appears as a lighter mobile phase which is taken to be the initial amount of metaplast.

Labile bridges either dissociate during pyrolysis or spontaneously decompose into char links. Consequently, bridge dissociation initiates two distinct reaction pathways, either to generate smaller fragments with new peripheral groups on the newly-created fragment ends, or to form a new char link and noncondensible gases. These pathways are designated as bridge scission and spontaneous condensation, respectively. Bridge scissions increase the amount of metaplast, at the expense of the reactant and intermediate, but spontaneous char formation tends to retain more of the coal mass in the heavier lumps, by lowering the number of sites available for fragmentation. Both reaction rates are based on the same Gaussian distribution of activation energies, and a stoichiometric coefficient specifies the selectivity between these two pathways.

Additional char links and noncondensible gases may also form by bimolecular recombination, but only within a restricted range of fragment sizes. Neither the reactant nor the intermediate species participate in bimolecular recombination, but nevertheless accumulate char links by spontaneous condensation. Recombinations among the ends of metaplast fragments produce additional char links, and also additional gases if peripheral groups are present on the ends which participate.

Tar formation is also developed from the metaplast only, using the flash distillation analogy; i. e., a phase equilibrium relates the instantaneous mole fractions of like fragments in the tar vapor and metaplast. Representing the equilibrium with Raoults law for continuous mixtures characterizes the impact of fragment size on the phase change. While no finite mass transport rates appear, all volatile species are presumed to escape by a convective flow process, so that the evolution rate of tar is proportional to that of noncondensibles when weighted by the ratio of their respective mole fractions.

Tar quality is expressed in terms of its molecular weight distribution, and the proportions of peripheral groups, labile and refractory links, as a coarse scale for aromaticity. Tar quality varies throughout the process, due in part to the greater impact of bimolecular recombination during the later stages.

Guidelines for the Data Correlations and Model Parameters

Taken together, the four laboratory studies[6-9] selected for the model evaluation depict the behavior for wide ranges of the relevant operating conditions, and all coal samples were Pittsburgh Seam HVA bituminous coals; ultimate and proximate analyses appear in the primary references. Among the results reported by Oh, only those which include tar yields and close the mass balance to within 5 wt% are included here. Wire-grid heaters in which the sample was dispersed in a layer which is only a few particles deep were used in all cases. Process temperatures were determined with fine-wire thermocouples and are regarded as the actual reaction temperature. One study featured forced rapid quenching, although decomposition during cooling is included in all simulations using the reported cooling rates.

All simulations in this study are based on the parameters in Table 1. The molecular weight of aromatic nuclei, and the MW ratios for bridges and peripheral groups were assigned from ^{13}C NMR analyses of HVA bituminous coals[10], to match the carbon

aromaticities and measured average molecular weights of noncondensibles (25g/g-mole). At the tabulated initial probability for all links, there is 9.4 wt % of metaplast in the reactant, which is similar to the amounts of THF extracts from such coals. All other values and the rate parameters were assigned to match the transient product distributions and tar molecular weights for atmospheric pyrolysis at 10^3K/s. Once assigned, only the operating conditions of pressure, temperature, heating rate, and/or time were varied to match those in all other experiments. While the pressure is usually assigned as the ambient pressure, simulations of vacuum pyrolysis are based on a pressure of 0.025 MPa.

A simulation of each thermal history requires about 2 minutes on a 386 personal computer operating at 20 MHz, with an 8-Bit Fortran compiler.

Data Correlations

The predicted distribution of all reaction species for atmospheric pyrolysis is compared with measured weight loss and tar yields in Fig. 1. The thermal histories consist of uniform heating at 10^3K/s to the stated temperatures immediately followed by cooling at 10^2K/s. The correlations of both weight loss and tar yields are within the experimental uncertainty throughout. Note that the proportions of tar to gas decrease continuously, and that tar formation is completed by about 900K, but gas evolution persists through higher temperatures.

The largest fragments in the coal, the reactant lump, are rapidly converted into intermediates up to about 950K. Note that, due to spontaneous char formation, not all of the reactant fragments dissociate into either of the smaller lumps. The intermediate accumulates continuously, initially by fragmentation of the reactant and ultimately by bimolecular recombination of metaplast. The predicted amount of metaplast is maximized at 800K, then falls during the most rapid stage of tar evolution; its disappearance coincides with the end of tar formation.

The predicted number-average molecular weight of tar for vacuum and atmospheric pressure are compared with Oh's measurements in Fig. 2. The predicted values for vacuum are within the experimental uncertainty, but seem low by several percent for the atmospheric tars. Notwithstanding, the theory captures the observations that (1) the first tar fragments are somewhat lighter than the bulk of the tar fraction; and (2) increasing the pressure shifts the tar to substantially lower molecular weights. Both of these features are tied to the flash distillation mechanism. Although predicted distributions are omitted here, they all are of the form of Gamma-distributions.

Variations in the thermal history for nearly-atmospheric pyrolysis are examined in Fig. 3. These three cases depict the influence of extended reaction times at constant temperature following uniform heating, and variations in heating rate of three orders of magnitude. For the case of heating at 10^3K/s with immediate quenching, the predictions are within the experimental uncertainty, except at the highest temperatures. The predicted impact of a 30 s reaction period at each temperature is qualitatively correct, in that most of the weight loss is observed at temperatures between 650 and 900K. But the predicted ultimate yields above 900 K are consistently lower than the data by about 6 wt %. As these investigators acknowledge[7], their ultimate yields are higher than the bulk of reported values for atmospheric pyrolysis, which are represented by the data in Fig. 1.

Similarly, the predicted variation due to lowering the heating rate from 10^3K/s to 1K/s is qualitatively accurate, and also within the experimental uncertainty for temperatures up to 800K. But at higher temperatures the predicted weight loss is about 12% lower than the data. We have not yet determined that raising the predicted yields at

10^3K/s would bring the predictions for 1K/s into quantitative agreement, although it would certainly improve the correlation.

This theory omits both gas-phase tar deposition and mass transport limitations which have long been regarded as the mechanistic basis for the pressure effect; instead, it relies on the phase equilibrium between metaplast and tar to retain more light fragments in the condensed phases as the pressure increases. This mechanism strongly influences the tar yields, especially at pressures up to several atmospheres. In Fig. 4, predicted tar yields at three pressures are validated by the available data.

An evaluation over a much wider pressure range, in Fig. 5, involves weight loss for extended reaction periods following heatup at 10^3K/s to 1025K. The quantitative discrepancies for pressures less than 5 atm are generally within 5 wt % of the data. Perhaps more importantly, the predicted approach to a near-asymptotic weight loss at pressures above 10 atm is clearly consistent with the data. The predicted tar yields (not shown) decrease with increasing pressure, but remain substantial at the highest pressures; e. g., at 10 atm, the predicted tar yield is 16 wt%. Predicted gas yields increase with increasing pressure, in accord with an established trend.

Discussion

Qualitatively, this theory captures the influences of all of the important operating conditions on the devolatilization behavior of high volatile bituminous coals, and in most cases the quantitative agreement is within the experimental uncertainties. But its greatest potential lies in the formalism to rationalize the behavior of different coals. In this study, only the connection to the structural parameters from ^{13}C NMR analyses has been demonstrated, and the general reliability of the predictions is encouraging. Future reports will evaluate the predicted behavior for variations in the parameters which describe the initial constitution of the coal.

Acknowlegement

References

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TABLE 1. MODEL PARAMETERS

Coal Characteristics

MW of Aromatic Nuclei	186 g/g-mole
MW Ratio, Bridges to Nuclei	0.785
MW Ratio, Char Links to Nuclei	0.300
MW Ratio, Peripheral Groups to Nuclei	0.134
Initial Fraction of Total Links	0.912
Initial Fraction of Labile Bridges	0.600

Rate Parameters

Reaction	A-Factor, s^{-1}	Ea, kJ/mole
Bridge Dissociation	3×10^{11}	176 ($\sigma = 25$)
Recombination	4×10^{14}	209
Per. Group Elim.	1×10^{15}	230

Selectivity Coefficient for Bridge Scission 0.35

$$P^{SAT}_{metaplast}(T, MW) = 1.5 \times 10^3 \exp(-165\ MW^{0.6}/T),\ MPa$$
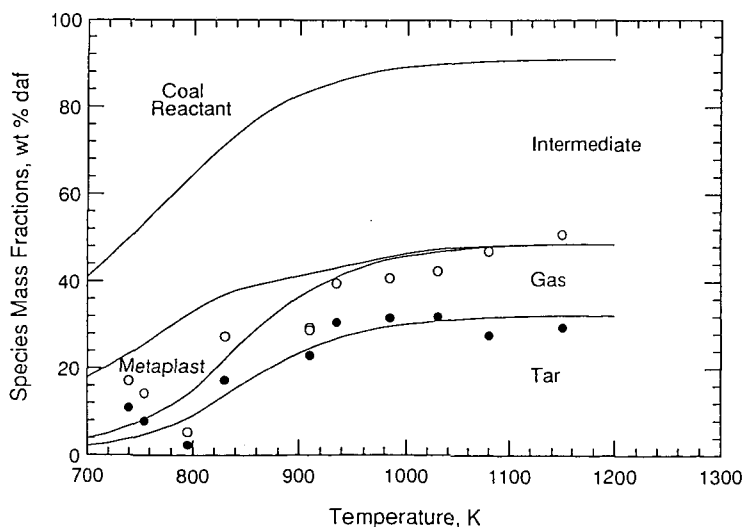
Fig. 1. The predicted distribution of reaction species for atmospheric pyrolysis for heating at 10^3K/s followed by immediate cooling at 100K/s, compared to Oh's[6] measurements of weight loss and tar yields.
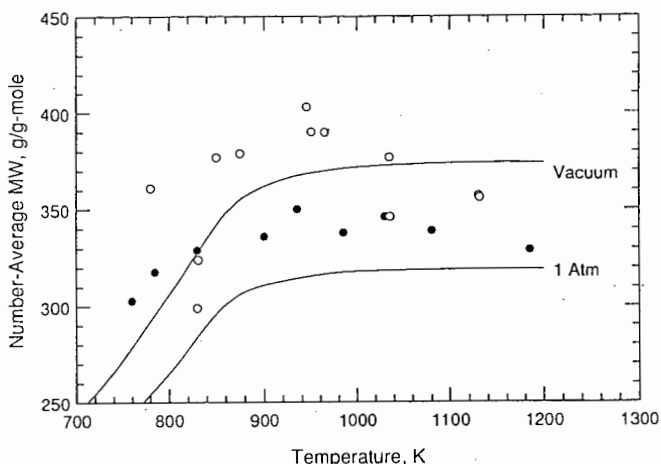
Fig. 2. An evaluation of the predicted number average molecular weights of tar for vacuum and atmospheric pyrolysis against Oh's[6] GPC determinations. Thermal histories are the same as in Fig. 1.
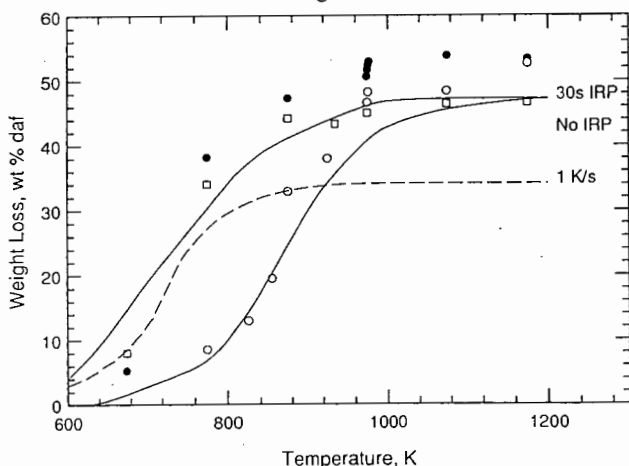

Fig. 3. An evaluation of the predicted weight loss for various thermal histories against the data recorded at 0. 12 MPa[7]. Both solid curves are for a heating rate of 10^3K/s, with different reaction times at constant temperature of 30s (upper curve and filled circles) and 0s (open circles). The dashed curve and open squares depict the behavior at 1K/s.
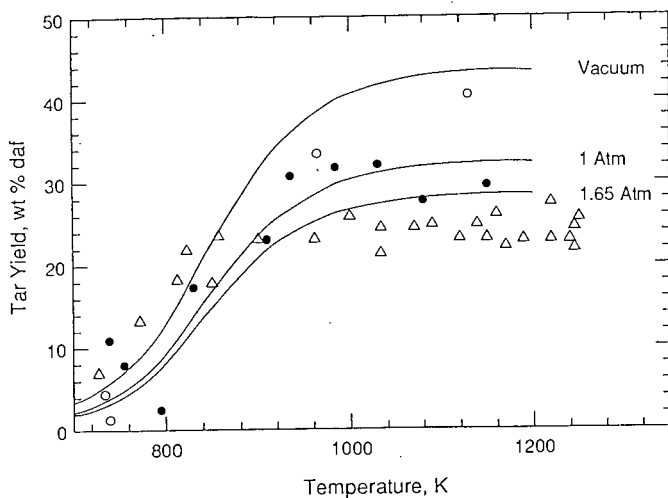
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Fig. 4. An evaluation of the predicted tar yields for vacuum and atmospheric pyrolysis, with data from Oh[6], and for pyrolysis at 0.165MPa, with data from Suuberg et al.[8] The thermal histories are the same as in Fig. 1.
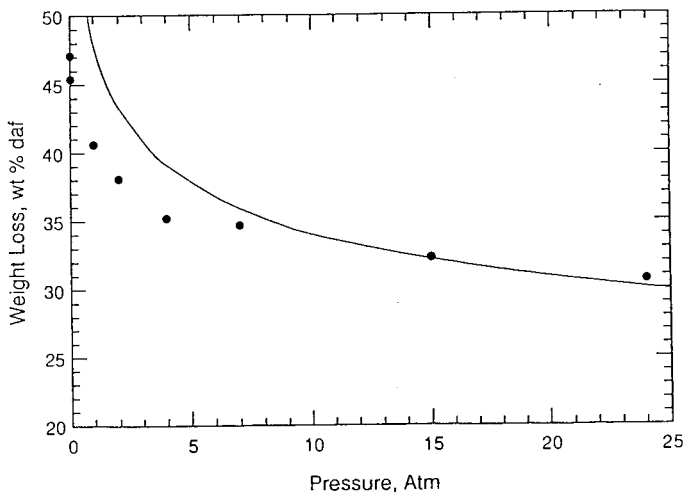

Fig. 5. An evaluation of the predicted weight loss at various pressures for heatup at 10^3K/s to 1025K with 10s reaction times. The data are from Bautista et al.[9]